The existence of the fine electronic structure in $LaCoO_3$

Z. Ropka

Center for Solid State Physics, św. Filip 5, 31-150 Kraków,

R.J. Radwański

Center for Solid State Physics, św. Filip 5, 31-150 Kraków; and

Inst. of Physics, Pedagogical University, 30-084 Kraków, Poland.

email: sfradwan@cyf-kr.edu.pl.

We argue that in $LaCoO_3$ exists the fine electronic structure associated with the atomic-like states of the Co^{3+} ions and caused by the crystal-field and intra-atomic spin-orbit interactions. This low-energy fine electronic structure has to be taken into account for any meaningful analysis of electronic and magnetic properties of $LaCoO_3$.

PACS No: 71.28 : 75.10.D : 71.70.Ej;

Keywords: Mott insulators, crystal-field interactions,

magnetic properties, $LaCoO_3$

Receipt date 10.02.1999 (Phys.Rev. B)

Properties of $LaCoO_3$, a non-magnetic ground state and an anomalous temperature dependence of the magnetic susceptibility (χ), are still intriguing despite of more than 30 years of intensive theoretical and experimental studies. See, Refs 1-8 and the current literature in Phys.Rev. B and Phys.Rev.Lett.

The aim of this short paper is to put attention that in $LaCoO_3$ the fine electronic structure exists. This fine electronic (f-e) structure is caused by the action of the crystal-field (CEF) and spin-orbit (s-o) interactions on the Co^{3+} ions.

The Co^{3+} ion has 6 electrons in the unfilled 3d shell. They form the highly-correlated electron system $3d^6$, the ground term of which is described[9,10] by S=2 and L=2 (^{5}D). Its 25-fold degeneration is removed by the CEF and the s-o coupling. In case of the dominancy of the CEF interactions over the s-o coupling, as is generally accepted for the 3d ions, we obtain for the quasi-octahedral site closely lying 15 levels originating from the $^5T_{2g}$ cubic

subterm [10]. Other 10 levels originating from the ^5E_g cubic subterm lie 2-3 eV above.

The existence of this fine electronic structure is generally neglected, see e.g. Refs 4-6, despite that the above-mentioned knowledge about the formation of the ^5D term can be found in text books[9]. This neglect of the f-e structure is in fact related with the neglection in the literature of the s-o coupling. We argue that the s-o coupling has to be taken into account for any meaningful analysis of electronic and magnetic (e-m) properties of compounds containing 3d ions like it is for rare-earth compounds[11–13]. This can be easily understood. The overall splitting of the $^5T_{2g}$ ground subterm by the s-o coupling amounts approximately to 5λ. With λ of $\mid 20\mid$ meV it means that there exists 15 discrete levels within the 100 meV range. It yields an average energy separation of 7 meV. The calculated by us the f-e structure of the Co^{3+} ion in the slightly distorted octahedral site, relevant to the situation realized in $LaCoO_3$, is shown in Fig. 1. There is the non-magnetic singlet (in the $|LSL_zS_z\rangle$ space) ground state and two excited doublets that turn out to be highly magnetic. These excited states become thermally populated with the increasing temperature.

The existence of such discrete levels affects electronic and magnetic properties, as we know well from rare-earth compounds[11–13]. In particular, some anomalies of the heat capacity (c) and of the magnetic susceptibility occur at temperatures comparable with the first energy separations. In the present case it is below 120 K ($\approx$ 11 meV). The experimentally observed anomalies in χ(T)[8] and c(T)[1] we are taking as the confirmation of the presence of the fine-electronic structure in $LaCoO_3$. The calculations[14], resembling those presented in Refs 11-13, reveal the Schottky-type maximum in the c(T) curve at about 60 K and the rounded maximum in the $\chi(T)$ curve at 90 K. The obtainable nonmagnetic ground state within the $^5T_{2g}$ subterm is very remarkable result. This subterm has been up to now considered as the source of the high-spin state only (compare please ref.15, p. 4258). The low-spin (i.e. nonmagnetic) state has been attributed to the $^1A_1$ term (Refs 15, 4). In contrary to the two-term consideration in the current literature, see Refs 4 and 15, in our calculations we get the low- and high-spin state within the one term (for it, the intra-atomic spin-orbit coupling is essentially important). Moreover, in the energy level scheme shown in Fig. 1

one can also find the origin for the intermediate-spin state (the first and the second excited states of Fig. 1 one can try to describe by the effective spin of 1.16 and 1.83, respectively - these values are somehow close to the ad hoc assumed values of S=1 and S=2 [Ref. 4]). These states are also in the discussed energy interval (up to 80 meV). The possibility of getting the non-magnetic ground state, discussed in the literature as the low-spin state, as well as the intermediate and highly-magnetic states within the same term we are taking as the great plus for our atomic-like approach. Surely the explanation involving one term only is phsically simpler to be realized. Moreover, according to the Occam's razor the simpler explanation is the better one.

In conclusion, we argue that in $LaCoO_3$ exists the fine electronic structure associated with the atomic-like states of the Co^{3+} ions and caused by the crystal-field (CEF) and intra-atomic spin-orbit (s-o) interactions. This fine electronic structure has to be taken into account for any meaningful analysis of electronic and magnetic properties of $LaCoO_3$. Our approach provides in the very natural way the non-magnetic low-temperature state (the $3d^6$ highly-correlated system is a non-Kramers system) and the insulating state in $LaCoO_3$. The present calculations correct the electronic-structure considerations presented in Refs 1-8. In particular, it turns out that the low-energy electronic structure is much more complex than that considered in Ref. 2 (Fig. 1) and points out the existence of the discrete states in contrary to the continuum energy-band structure derived in Ref. 6 (Figs 1 and 2), in Ref. 4 (Figs. 1-3, 7) and in Ref. 5.

The note added during the referee process (15.05.2000). 1. The present discussion of $LaCoO_3$ differs significantly from the conventional one when the low-spin nonmagnetic state $^1A_1$ is realized for strong enough crystal fields. Our nonmagnetic state is found within the weak crystal-field regime, i.e. when the crystal field does not break the intra-atomic arrangement. 2. We would like to point out that our approach should not be considered as the treatment of an isolated ion only - we consider the Co^{3+} ion in the oxygen octahedron. The physical relevance of our treatment to $LaCoO_3$ is obvious - the perovskite structure is built up from the corner sharing Co^{3+} octahedra. 3. We do not agree with the referee that the

splitting of only 11 meV can be easily exceeded by the exchange interaction between Co ions leading to the magnetically-ordered ground state of $LaCoO_3$. As the confirmation of our approach we can mention that the temperature dependence of the paramagnetic susceptibility resulting from our approach [16] reproduces very well the one observed for $LaCoO_3$. 4. The present approach, pointing out the existence of the discrete energy spectrum, fundamentally differs from the continuum energy-band structure considerations discussed recently in Ref. 17.

Acknowledgement.The authors are grateful to R.Michalski for the technical assistance.

---

[1] S.Stølen, F.Grønvold, H.Brinks, T. Atake and H.Mori, Phys.Rev. B 55 (1997) 14103.

[2] M.R. Ibarra, R.Mahendiran, C.Marquina, B. García-Landa and J.Blasco, Phys.Rev. B 57 (1998) R3217.

[3] S.Yamaguchi, Y.Okimoto, H.Taniguchi and Y.Tokura, Phys.Rev. B 53 (1996) R2926.

[4] M.A. Korotin, S.Yu.Ezhov, I.V.Solovyev, V.I.Anisimov, D.I.Khomskii and G.A.Sawatzky, Phys.Rev. B 54 (1996) 5309.

[5] N.Solovyev, N.Hamada and K.Terakura, Phys.Rev. B 53 (1996) 7158.

[6] M.Zhuang, W.Zhang, C.Hu and N.Ming, Phys.Rev. B 57 (1998) 10710.

[7] D.D.Sarma, N.Shanti and P.Mahadevan, Phys.Rev.B 54 (1996) 1622.

[8] K.Asai, A.Yoneda, O.Yokokura, J.M.Tranquada, G.Shirane and K.Kohn, J.Phys.Soc.Japan 67 (1998) 290.

[9] A.Abragam and B.Bleaney, in: Electron Paramagnetic Resonance of Transition Ions, (Clarendon Press, Oxford) 1970; C.J.Ballhausen, in: Ligand Field Theory (McGraw-Hill Comp.) 1962; W.Low, in: Paramagnetic resonance in solids (Academic Press) 1960; B.N.Figgis, in:

Introduction to ligands fields (Interscience Publ.) 1966.

[10] R.J.Radwanski and Z.Ropka, Relativistic effects in the electronic structure of the 3d paramagnetic ions - http://xxx.lanl.gov/abs/cond-mat/9907141.

[11] R.J.Radwański, J.Phys.:Condens.Matter 6 (1994) L15.

[12] R.J. Radwański, N.H. Kim-Ngan, F.E. Kayzel, J.J.M.Franse, D.Gignoux, D.Schmitt and F.Y.Zhang, J.Phys.:Condens.Matter 4 (1992) 8859.

[13] R.J.Radwański and J.J.M.Franse, J.Magn.Magn.Mater. 80 (1989) 14.

[14] the computer program can be obtained on the written request to the authors

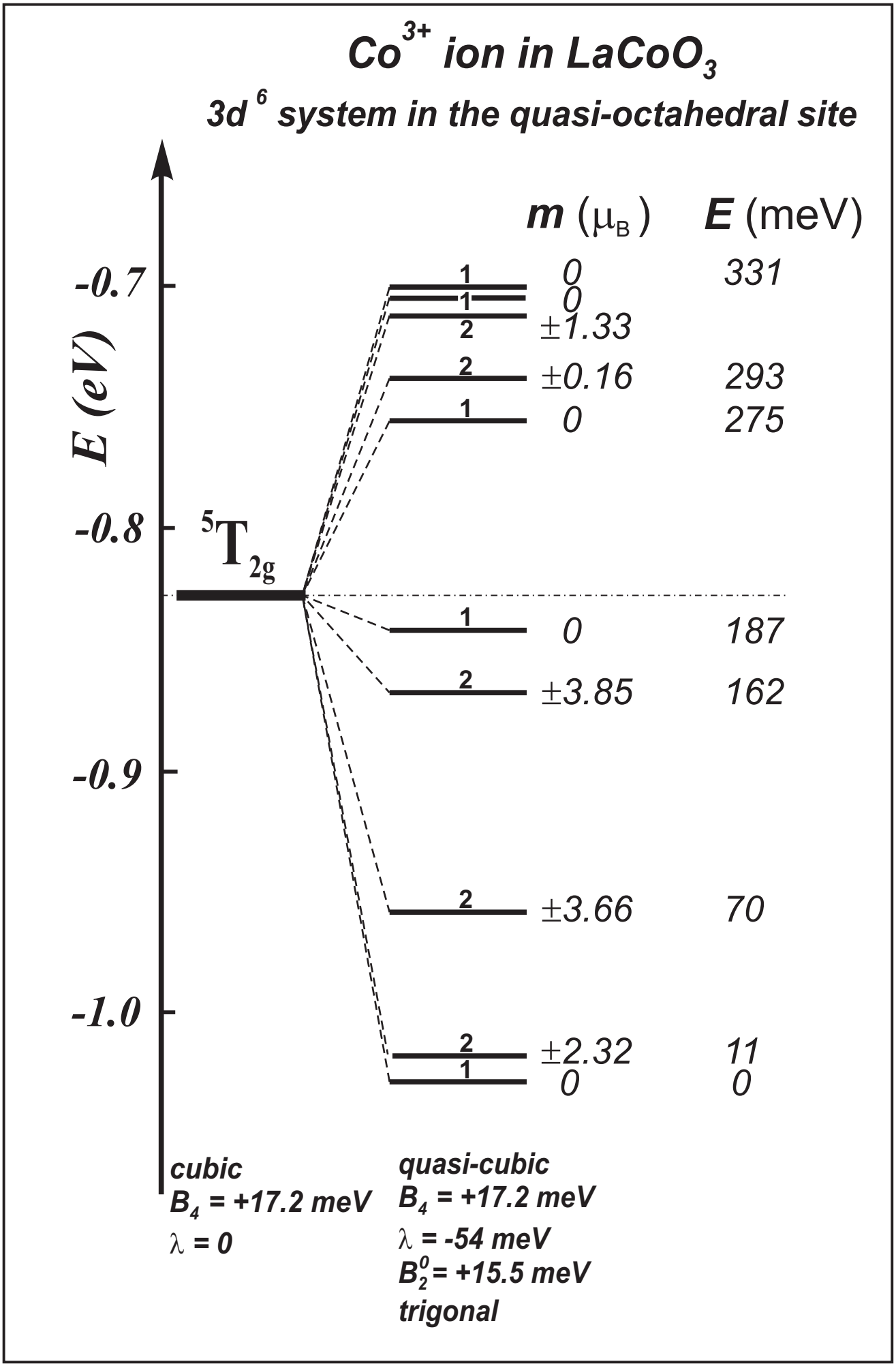
[15] T.Saitoh, T.Mizokawa, A.Fujimori, M.Abbate, Y.Takeda and M.Takano, Phys.,Rev. B 55 (1997) 4257.

[16] R.J.Radwanski and Z.Ropka, Solid State Commun. 112 (1999) 621.

[17] P.Ravindran, P.A.Korzhavyi, H.Fjellvag and A.Kjekshus, Phys.Rev. B 60 (1999) 16423.

Figure caption:

Fig. 1. The lowest part of the fine electronic structure of the Co^{3+} ion in $LaCoO_3$ originating from the cubic subterm $^5T_{2g}$. Other 10 states of the ^5D term originating from the ^5E_g cubic subterm are 2.0-3.0 eV above - they practically do not influence the magnetic and electronic properties of $LaCoO_3$. The non-magnetic ground state as well as the intermediate and high-magnetic states should be noticed in this atomic-like fine electronic structure.


Co3+ ion in LaCoO3
3d 6 system in the quasi-octahedral site
m (μB)
E (meV)
E (eV)
-0.7
-0.8
-0.9
-1.0
5T2g
1
0
331
1
0
2
±1.33
2
±0.16
293
1
0
275
1
0
187
2
±3.85
162
2
±3.66
70
2
±2.32
11
1
0
0
cubic
B4 = +17.2 meV
λ = 0
quasi-cubic
B4 = +17.2 meV
λ = -54 meV
B20 = +15.5 meV
trigonal